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Behaviour of nickel, copper, zinc and cadmium in the upper 300 m of a transect in the Southern Ocean (57°–62°S, 49°W)

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Abstract

The distributions of Ni, Cu, Zn and Cd in relation to phosphate, nitrate and silicate in the upper 300 m of a transect in the Southern Ocean were studied. This transect covers the Scotia Sea, the Confluence and the Weddell Sea. These three watermasses are clearly separated by their temperature and salinity regimes. Also, the nutrients show different concentration gradients, with that of silicate most pronounced, with concentrations decreasing from 60–80 μM in the Weddell Sea to 20–30 μM in the Scotia Sea. Below 100 m, Cd concentrations are high in the Scotia Sea ($\sim$ 0.8 nM) and lower ($\sim$ 0.6 nM) in the Weddell Sea, but there is still a strong covariance with phosphate. The Cd/phosphate ratio is, however, different in each of the three areas. In contrast with Cd the Cu concentrations are lower ($\sim$ 2 nM) in the Scotia Sea and higher ($\sim$ 5 nM) in the Weddell Sea, and show some relation with silicate. Zn shows the same distribution pattern as Cd, and the relation with silicate is specific for each of the three regions on its own. The distribution of Ni is more complex, but the highest concentrations (8 nM) appear to be in the upper surface layer (200 m) of the Scotia Sea. Lower concentrations (4 nM) are found in the Weddell Sea. Some covariation with the nutrients is found for Ni. It is shown that the surface waters in the turbulent area around the Antarctic Peninsula are not only characterized by their salinity, temperature and nutrient properties, but also by different trace metal contents. In each of the three areas, the differences in the actual concentrations are more dependent on the time of sampling (receding ice-edge, primary production) than on the exact sampling position.

1. Introduction

The involvement of trace metals such as Cd, Cu, Zn and Ni in the marine biogeochemical cycle is not well understood (Morel and Hudson, 1985; Price and Morel, 1990). Due to improved techniques for sampling, and handling of seawater for trace-metal determinations, our knowledge of their geochemical behaviour has increased. Most of the investigations were, however, concentrated in the Northern Hemisphere (e.g. Boyle et al., 1976, 1981; Martin et al., 1976; Bruland, 1983; Bruland and Franks, 1983; Yeats, 1988). Before 1985 reports on trace-metal distributions in the Southern Ocean (Antarctica) were scarce (Harris and Fabris, 1979). Since then, more attention has been given to this remote and, in respect of trace metals, pristine area (Orren and Monteiro, 1985; Bordin et al., 1987; Martin et al., 1990; Nolting and de Baar, 1990; Westerlund and Öhman, 1991a,b; Nolting et al., 1991). The gap that existed between the data available from the northern part and the Southern Hemisphere of the oceans is partly filled with these new results.

Whereas in oligotrophic surface waters metals and nutrients are often depleted, this is not the case in Antarctic waters. Nor is it in other nutrient-rich surface waters, for example the northwest Indian Ocean (Saager et al., 1992) and the northern NE-Pacific Ocean (Martin et al., 1989). It is important to gather more insight and increase our knowledge of the processes regulating the distribution and interactions of

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these parameters, where remote areas like the Antarctic Ocean may yield new insights.

For this reason we investigated surface waters of the Scotia Sea, Scotia/Weddell Confluence and the northern Weddell Sea. For each of these regions water samples were collected at two stations at discrete depths, in the upper 300 m of the water column, because in the upper water column biologic processes have a major impact on nutrient, salinity, temperature and trace-metal distributions, where in this region the receding ice-edge and the subsequent wind-induced increase of the mixed surface layer play a major role. Results for Cd, Cu and Fe in the very surface layer and some depth profiles from the same regions were published earlier (Nolting et al., 1991). Here we discuss the relationship between dissolved Cu, Cd, Zn and Ni and nutrients in the upper watercolumn. This research was a part of the EPOS (European Polarstern Study) programme organized by the European Science Foundation in close co-operation with the Alfred Wegener Institute for Ocean and Polar Research.

2. Sampling and methods

Samples were collected from 26 November 1988 to 4 January 1989 during a survey with the RV *Polarstern* using 12 well-cleaned, modified, Teflon-coated Go-Flo samplers (12 l volume) on an all Teflon-coated stainless steel CTD/Rosette frame. The cruise track together with the station numbers is presented in Fig. 1. The selected stations were 151 and 153 (almost fully ice-covered) in the Weddell Sea, 158 and 174 in the Confluence and 182 and 186 in the Scotia Sea (no ice cover) (Table 1). Due to logistics, the time gap between station 158 and 174 in the Confluence was 14 days. This means that sampling at station 158 took place in the outer marginal ice zone (ice cover 20%) and at station 174 where the ice cover was 0% (van Franeker, 1992). Surface samples were collected with a rubber zodiac when possible. The Rosette was always sent down to depths greater than 500 m

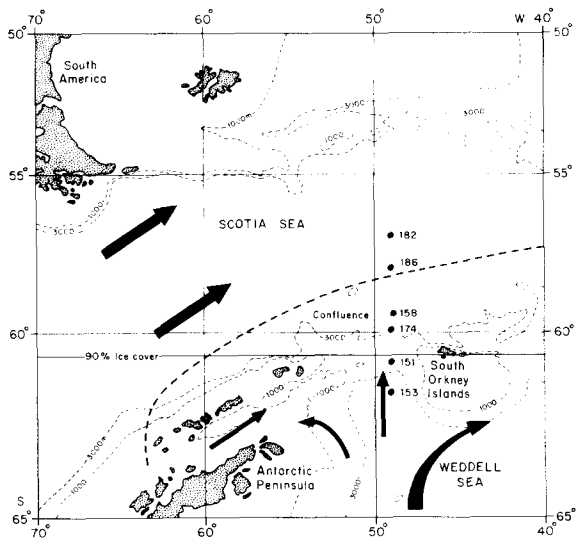

Fig. 1. Map of the study area with sampling positions indicated. Dashed line indicates the southern boundary of the Antarctic circumpolar current.

to flush out any possible contamination, while during the upcast the samplers were closed at selected depths. At least 13 depths were sampled in the upper 300 m. Upon recovery, the samplers were mounted outside a Class-100 clean air laboratory container. The samplers were connected with all-Teflon (PTFE, FEP) tubing leading the water inside the laboratory container, where it was fed through all-Teflon filtering units. Under nitrogen pressure the seawater was filtered over acid cleaned 0.4 μm Nuclepore filters. The first liters of seawater were discarded and subsequently a precleaned, 1 l polypropylene bottle was rinsed threefold with the sample and then filled with the filtered seawater. Thereafter the samples were acidified inside laminar flow benches with 1 ml 12 *N* HCl, packed in plastic bags and stored for analyses. Surface samples were not filtered but otherwise also acidified and processed as below (Nolting, 1986).

After a few days, the seawater samples were subjected to an APDC/DDDC freon extraction in Teflon separatory funnels, back extracted in HNO_3 and stored in 30 ml Teflon flasks (Danielsson et al., 1978, 1982). Using 500 ml of seawater sample and a final back extraction

Table 1
Sampling depth, hydrography, nutrients and trace metal results of EPOS Stations 151, 153, 158, 174, 182 and 186

Depth (m)	T (°C)	Salinity (‰)	PO_4 (μM)	NO_3 (μM)	Si (μM)	Cu (nM)	Cd (nM)	Zn (nM)	Ni (nM)
Station 151 [60°58.8′S, 49°03.1′W]									
0.000						(4.63)[a]	0.58	(12.39)	(10.26)
10.000	−1.733	34.185	2.06	30.8	77.2	3.80	0.56	(12.39)	6.12
20.000	−1.758	34.196	2.07	30.9	77.1	3.54	0.53	9.17	6.46
40.000	−1.795	34.237	2.08	31.0	77.2		0.58		
60.000	−1.810	34.279	2.07	31.7	78.1		0.61		6.90
80.000	−1.812	34.324	2.09	31.8	77.8	3.20	0.60	4.43	5.91
100.000	−1.808	34.368	2.09	32.1	77.3	4.47	0.54	5.05	6.08
120.000	−1.715	34.418	2.12	32.8	79.8	2.71	0.56	6.27	6.05
150.000	−1.359	34.462	2.15	33.0	84.4	2.88	0.56	8.56	
200.000	−0.660	34.552	2.21	33.7	92.6	4.91	0.60	11.62	6.01
300.000	0.181	34.650	2.27	34.5	105.5	4.01	0.55	10.55	
Station 153 [61°59.7′S, 48°59.6′W]									
10.000	−1.809	34.312	2.01	30.9	76.5	4.17	0.40	6.12	4.60
20.000	−1.809	34.312	2.00	30.9	77.3	3.48	0.47	6.42	4.09
40.000	−1.812	34.320	2.01	31.0	77.3	2.85	0.40	5.81	
60.000	−1.809	34.353	2.02	31.2	77.9	2.93	0.43		4.26
80.000	−1.797	34.375	2.03	31.5	78.0	2.74	0.43	9.02	3.75
100.000	−1.741	34.409	2.04	31.7	79.2	4.38	0.41	(11.93)	4.26
120.000	−1.496	34.462		31.7	82.5	6.44	0.50	(16.82)	3.07
150.000	−1.098	34.503	2.14	32.9	88.0	5.24	0.56	(20.18)	3.75
200.000	−0.323	34.598							
300.000	0.316	34.669	2.26	34.3	108.4	4.04	0.55	(14.68)	9.71
Station 158 [59°22.3′S, 48°44.2′W]									
0.000			1.49	25.3	68.0	3.53	0.48		(13.29)
10.000	−1.210	33.488	1.49	25.1	67.7	4.69	0.41	4.74	4.77
20.000	−1.261	33.543	1.53	26.1	68.0	5.37	0.50	5.20	
30.000	−1.421	33.790				4.17	0.48	5.05	5.11
40.000	−1.424	33.856	1.84	29.1	72.2	3.17	0.48	5.35	4.94
50.000	−1.481	34.020				2.61	0.51	5.50	5.11
60.000	−1.454	34.103	1.99	31.6	76.4	2.80	0.55	5.20	
80.000	−1.389	34.228	2.09	33.0	80.1	3.56	0.63		
100.000	−1.335	34.282	2.15	35.0	83.8	2.91	0.64	6.73	5.45
120.000	−1.083	34.353	2.16	35.5	86.3	4.68	0.64	8.26	5.79
150.000	−0.896	34.388	2.18	36.3	87.2	3.56	0.65	7.49	5.11
200.000	−0.237	34.506	2.21	37.0	90.3	3.04	0.61	7.49	7.16
300.000	0.175	34.581	2.21	36.6	96.3	4.47	0.57	9.48	4.60
Station 174 [59°59.5′S, 48°58.8′W]									
0.000			1.85	28.9	81.5	2.00	0.53	6.12	8.33
10.000	−0.644	33.876	1.83	29.0	82.3	2.65	0.58	8.56	
20.000	−0.950	33.909	1.88	29.9	84.0	2.94	0.56	9.94	
30.000	−1.357	34.070	2.00	31.4	84.6	2.27	0.61	10.86	9.03
40.000	−1.436	34.090	2.02	31.3	82.8	2.27	0.65	8.10	8.16
50.000	−1.503	34.116	2.07	31.7	82.4	2.08	0.65	9.02	
60.000	−1.532	34.218	2.09	32.8	84.0	1.59	0.72	9.33	8.45
80.000	−1.521	34.294	2.18	33.6	86.9	2.05	0.67	10.24	
100.000	−1.516	34.309	2.15	33.7	86.6	3.04	0.73	12.23	10.36
120.000	−1.468	34.339	2.15	33.9	87.1	2.80	0.66		7.96
150.000	−1.307	34.396	2.16	33.9	88.3	2.89	0.67	12.84	10.39
200.000	−1.126	34.449	2.19	34.3	91.2	2.94	0.76		9.85
300.000	0.054	34.585	2.23	34.6	98.2	1.92	0.78	12.54	8.98

Table 1 (continued)

Depth (m)	T (°C)	Salinity (‰)	PO_4 (μM)	NO_3 (μM)	Si (μM)	Cu (nM)	Cd (nM)	Zn (nM)	Ni (nM)
Station 182 [57°02.9′S, 48°50.9′W]									
0.000			1.60	26.4	15.0	1.91	0.41	6.57	
10.000	3.085	33.805	1.60	26.4	15.0	2.44	0.17	6.27	8.52
20.000	2.330	33.797	1.65	27.0	16.0	2.30	0.19	2.14	
30.000	2.251	33.805	1.66	27.2	17.0	1.53	0.23	1.68	6.47
40.000	2.073	33.816	1.74	27.9	19.0		0.53		
50.000	1.631	33.833	1.76	28.2	20.5	1.84	0.53		
60.000	0.798	33.847	1.80	28.6	23.0	1.48	0.43	1.83	7.50
80.000	−0.074	33.887	2.01	30.3	25.0	1.81	0.53	3.36	7.84
100.000	−0.049	33.954	2.09	32.2	29.5	1.81	0.57	3.21	6.13
120.000	0.334	34.026	2.18	34.0	36.5	1.87	0.81		
150.000	0.972	34.139	2.28	35.8	41.5		0.74	5.35	
200.000	1.430	34.234	2.37	37.2	50.0	1.81	0.85		
300.000	1.763	34.381	2.50	38.9	64.0	1.81	0.89	7.34	7.67
Station 186 [58°00.0′S, 48°59.0′W]									
10.000	2.043	33.817	1.76	27.0	32.9	1.94	0.39	1.38	6.81
30.000	0.999	33.784	1.86	28.3	36.9	2.47	0.41	1.38	8.18
40.000	0.039	33.899	1.89	28.5	36.2	2.57	0.46	1.68	6.98
50.000	−0.132	33.911	1.88	28.6	35.8	2.57	0.41	4.59	7.33
60.000	−0.152	33.900	1.89	28.8	34.1	(4.14)	0.87	9.48	
80.000	−0.374	34.054	2.13	31.9	42.4	3.21	0.66	8.41	8.52
100.000	0.045	34.146	2.26	34.3	56.0	3.38	0.71	8.87	7.50
120.000	0.624	34.245	2.39	36.1	64.5	(5.18)	0.87	13.91	7.50
150.000	1.112	34.317	2.47	36.8	71.6	2.43	0.80	11.77	
200.000	1.809	34.475	2.46	36.6	77.3	3.34	0.80	11.62	8.01
300.000	1.931	34.595	2.42	36.0	85.2	3.54	0.95	9.37	

[a]Values between brackets suspected of contamination.

volume of 5 ml, a concentration factor of 100 was obtained. The flasks were stored in a refrigerator until analysis in the shore laboratory. There the extracts were analysed with a Perkin Elmer 5100 Zeeman AAS, using the platform technique against standards in 0.1 *N* HCl. Relative standard deviation for 6 replicates was Cu 2.2%, Ni 3.9%, Zn 2.2%, and Cd 6.2 %. Throughout the procedures only extensively acid-cleaned and rinsed Teflon and Polyethylene labware was used. All reagents were sub-boiled quartz distilled. Blanks were Cu 0.16 nM, Cd 0.006 nM, Ni 0.43 nM, and Zn 0.23 nM and were corrected for. In 1989, we participated with this method for all four metals as well as Pb in the seawater trace-metal certification program CRM-402 of the EEC (Quevauviller et al., 1992). In the final certification round, the results presented to the EEC, for all mentioned metals, were accepted for use in the certification of this reference material.

Analyses of nutrients were done on shipboard with standard methods and can be found together with hydrographical data in a NIOZ data-report (EPOS-Leg 2, 1991).

3. Hydrography

The northern part of the research area is the Scotia Sea, which is characterized by high surface temperatures and low surface salinities (Fig. 2). This area has a distinct temperature minimum at 60–70 m depth, which is characteristic of the winter water, and from 200 m downwards the temperature is rather constant. This area belongs to the Antarctic Circumpolar Current

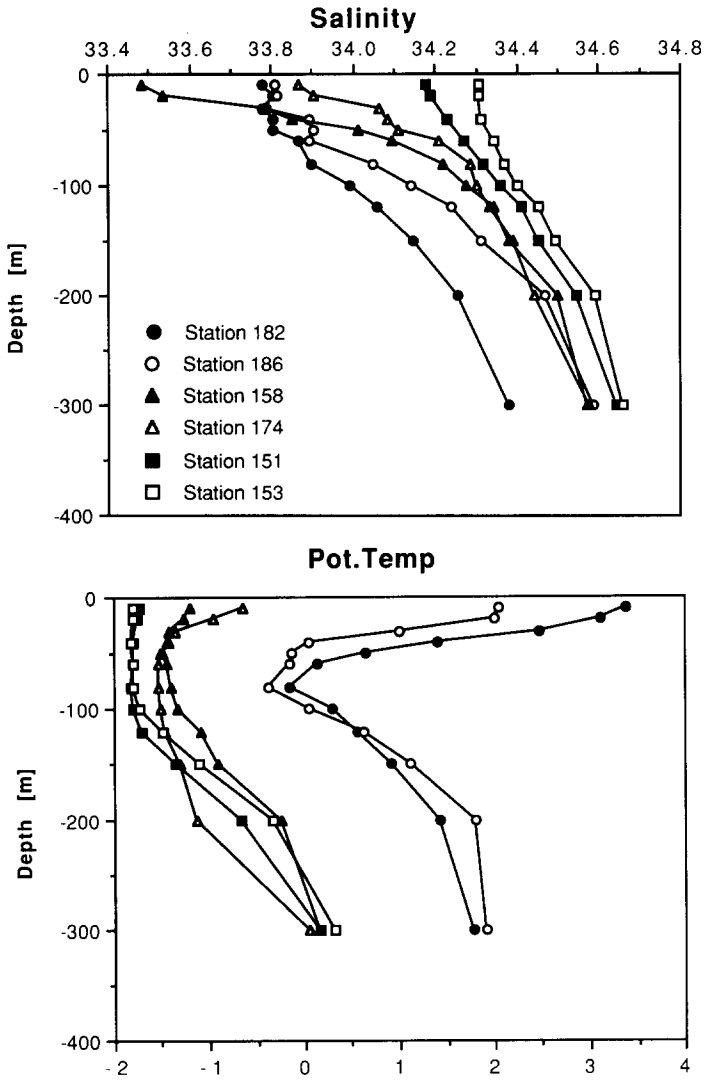

Fig. 2. Profiles of salinity and potential temperature in the top 300 m of the research area. Stations 182 and 186 (circles) in the Scotia Sea, stations 158 and 174 (triangles) in the Confluence, and stations 151 and 153 (squares) in the Weddell Sea.

proper. More southward one finds the transition into the Scotia/Weddell Confluence with lower surface temperatures (below 0°C) and higher salinities at station 174 but lower at station 158 due to meltwater of ice and snow (Fig. 2). This area is the complex mixing zone of water masses from the Scotia Sea, the Weddell Sea and those passing the Gerlache Strait and the Bransfield Strait. The most southern part of the research area is the ice-covered Weddell Sea, with lowest surface temperatures and highest salinities. Due to the high ice cover there is hardly any wind-mixed layer, resulting in a water body of 100 m depth with an almost constant temperature of −1.7°C, below which stratification occurred (Fig. 2). This part of the Weddell Sea is characterized by the Weddell Gyre, which flows northeastward. As a result of the complex and dynamic mixing between the two currents, the hydrography of the Confluence is rather dynamic or even slightly chaotic (Cederlöf et al., 1989). It is, however, clear that the three

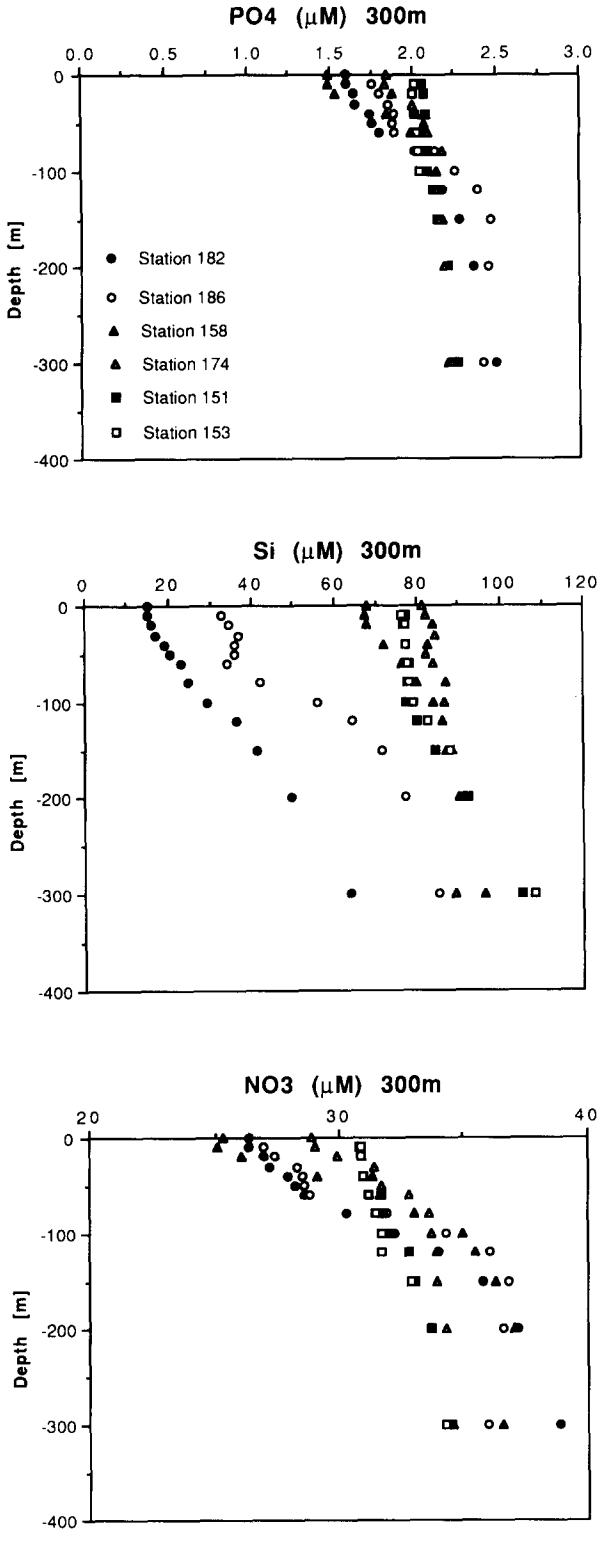

Fig. 3. Profiles of phosphate, nitrate and silicate (μM). For locations of stations see Fig. 2.

areas are distinct in having their own different temperature and salinity regimes.

4. Results and discussion

4.1 Nutrients

The profiles of nitrate, phosphate and silicate are given in Fig. 3. Phosphate and nitrate show some surface depletion, with strong gradients being found in the Scotia Sea, stations 182 and 186. This is in contrast to stations 151 and 153, situated in the Weddell Sea, where concentration gradients are smaller in the upper 300 m. The strongest surface depletion is, however, observed at station 158 in the Confluence, where also the lowest salinity is found. This is the station where the marginal ice zone is receding, contributing melt water from the ice-edge to the surface layer and also inducing an event of higher primary production. Below 100 m, concentrations of phosphate and nitrate increase slightly. The profiles reflect that of salinity, indicating a strong coupling with hydrography. In Fig. 4, the relation between phosphate and nitrate of all stations is given. There exists a good correlation between these nutrients in the different water masses and the ratio of 14.6 is typical for the Antarctic Ocean which is slightly below the ratio of 16 estimated as average for oceanic waters by Redfield et al. (1963).

Silicate exhibits stronger surface concentration gradients, with the highest surface concentrations (60–80 μM) in the Weddell Sea and Confluence and lower concentrations (20–30 μM) and steeper depth gradients in the Scotia Sea. The differences in nutrient concentrations together with those of salinity and temperature in the upper 300 m indicate that we are dealing with three distinct water masses. This is obvious from plotting silicate and phosphate against salinity (Fig. 5). There is a clear shift in silicate concentrations at salinities lower than 34.4. Where in the Scotia Sea silicate and salinity are

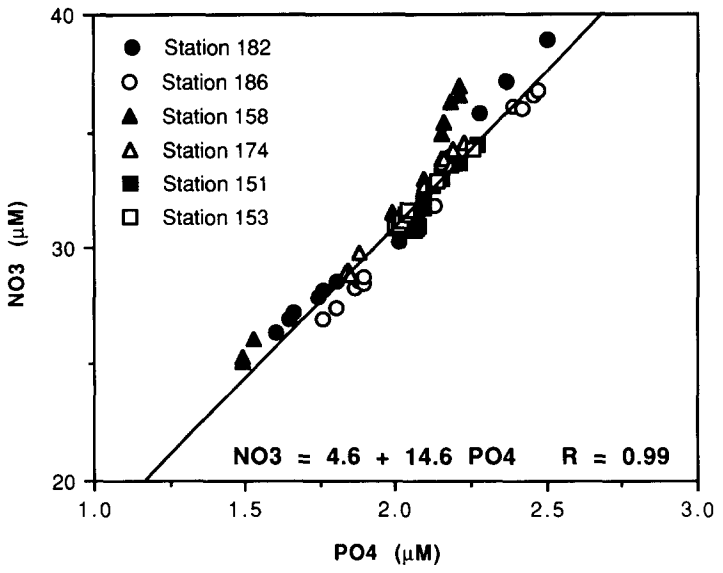

Fig. 4. Relation between nitrate and phosphate. For locations of stations see Fig. 2.

related to each other with a steep slope, this is not the case in the Confluence and Weddell Sea. In the latter regions the variations in silicate concentrations are small, and only at salinities higher than 34.4 the silicate increases. It is obvious that at equal salinities the silicate concentrations are different in the Scotia Sea and the Confluence.

Phosphate concentrations are lower in the Weddell Sea than in the Confluence at the same salinities, but in both regions the inter-relationship with salinity is good. The phosphate concentrations in the Scotia Sea are clearly higher than those in the Confluence and Weddell Sea at the same salinities, and show the surface depletion as discussed above.

From these observations it can be concluded that our stations situated in the Scotia Sea receive water from the Circumpolar Current passing the South Drake Passage (Whitworth, 1988; data from Martin et al., 1990). Waters at the stations in the Confluence are a mixture of water from the Gerlache Strait, Bransfield Strait, Weddell Sea, melt water from sea ice and icebergs and upwelling water from the Drake Passage. Surface water in the Weddell Sea is derived from ice-shelf water from the southern part of the Weddell Sea (data from Westerlund and Öhman, 1991a,b).

4.2 Trace metals

The profiles of dissolved Ni, Cu, Zn and Cd in the upper 300 m of the N–S transect are shown in Fig. 6 and element/salinity plots in Fig. 7. All relevant data are given in Table 1. Zn and Cd show almost similar trends as the nutrients, lower concentrations at the surface, then increasing with depth. Their nutrient-like distribution has been reported extensively (Boyle et al., 1976, 1977; Bruland, 1983; Danielsson et al., 1985; Kremling, 1985; Nolting et al., 1991; Westerlund and Öhman, 1991b; Saager et al., 1992; de Baar et al., submitted). Ni and Cu are also known to be incorporated in the biogeochemical cycle (Bruland, 1983), but this trend is not so obvious in our findings.

Cd

Cd concentrations range from 0.2 to 0.6 nM at or near the surface and from 0.5 to 0.9 nM at 300 m. Higher concentrations are found deeper in the Scotia Sea. The Cd/salinity plot (Fig. 7) gives more information about the water sources with

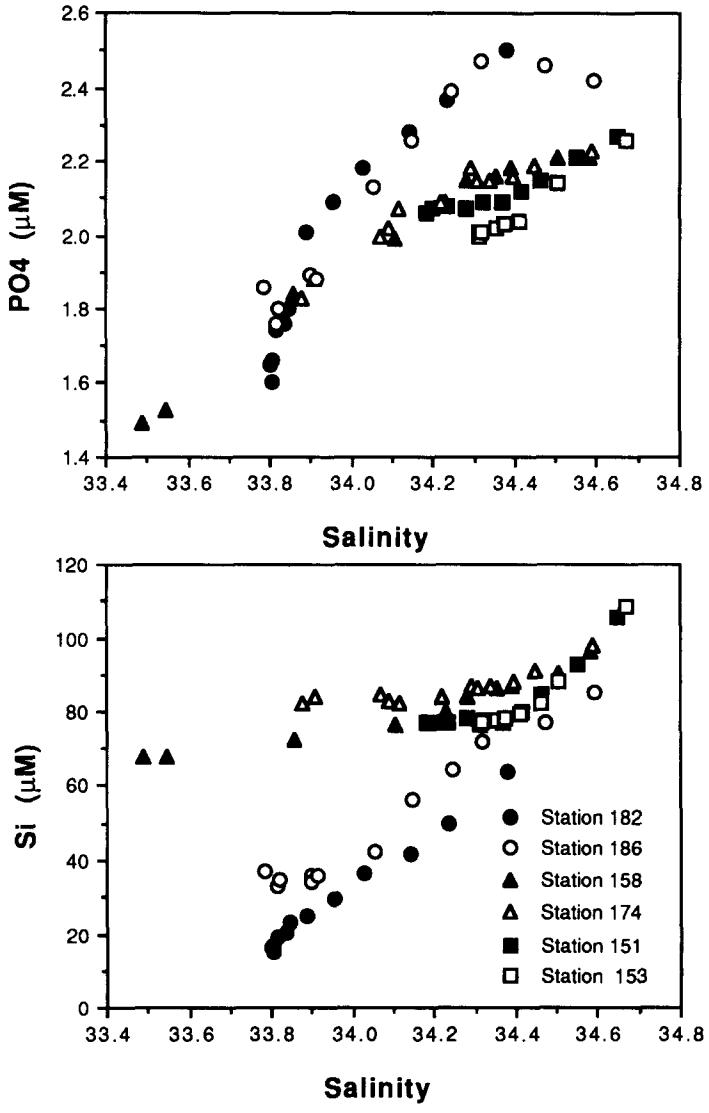

Fig. 5. Relation between salinity, phosphate and silicate (μM). For locations of stations see Fig. 2.

which we are dealing, in the same way as salinity against phosphate and silicate. The Cd concentrations and all other parameters (salinity, nutrients) at station 182 (Scotia Sea) resemble those reported by Martin et al. (1990) for their South Drake Passage station. The similar comparison for the Confluence (stations 158 and 174) indicates a strong influence from water arriving from the Gerlache Strait (Martin et al., 1990). Cd concentrations and salinity in the Weddell Sea are comparable with those reported by Westerlund and Öhman (1991b).

Relations between Cd and phosphate for the complete depth profiles can be found in Nolting et al. (1991). The Cd phosphate relation in deep waters of the oceans is extensively discussed by de Baar et al. (submitted). Cd phosphate relations from this transect are given in Fig. 8. The correlation is represented by the equation:

$$\mathrm{Cd\,(nM)} = 0.55\,\mathrm{PO_4\,(\mu M)} - 0.53$$
$$(R = 0.83,\ n = 53)$$

At first glance the relation appears similar to

earlier reported relations for this region (Nolting et al., 1991). However, on close inspection some special features become apparent. The slope of the data from the Scotia Sea is 0.62 and steeper than that from the Confluence (0.50) while values in the Weddell Sea are narrowly ranged. Such clustering was also observed by Westerlund and Öhmann (1991b). Plotting the molar ratio Cd/PO_4 against depth (Fig. 9) it is evident that this ratio is rather constant in the Confluence (0.3×10^{-3}) and Weddell Sea ($0.2-0.3 \times 10^{-3}$), but increases with depth in the Scotia Sea ($0.1-0.4 \times 10^{-3}$). Such increase with depth of the molar ratio Cd/PO_4 is commonly observed in the upper water column of all other oceans (Saager et al., 1992; Frew and Hunter, 1992; Morley et al., 1993; De Baar et al., submitted). Below 100 m, the ratio is almost constant and shifts from 0.40×10^{-3} in the Scotia Sea to 0.25×10^{-3} in the Weddell Sea. This indicates that the utilization of phosphate and Cd (in the first 300 m) in the Confluence and Weddell Sea takes place at the same rate. In the Scotia Sea, Cd is removed more efficiently from the surface layer than phosphate or phosphate remineralisation is much faster than that of Cd. This is also indicated by the more negative intercept −0.65, if the Cd–phosphate relation is plotted for the Scotia Sea stations only. The intercept here is more negative than at higher latitudes where on the other hand the slopes are less steep (e.g. Bruland et al., 1978a; Bruland, 1980; Knauer and Martin, 1981; Danielsson and Westerlund, 1983; Nolting and de Baar, 1990). Recently, Frew and Hunter (1992) reported low Cd–phosphate ratios at a Subantarctic station (48°05′S, 164°30′E), northwards of the Antarctic Ocean proper for which Cd/phosphate data were previously published (Westerlund and Öhman, 1991a,b; Nolting et al., 1991, and references therein). They suggested that this low ratio was a clear signal of Antarctic Intermediate Water (AAIW) and that Antarctic and Subantarctic waters are influenced by a common process that generates low Cd/phosphate ratios. Only for the upper water column of the Antarctic Ocean proper these low $Cd-PO_4$ ratios had indeed been reported previously (Nolting et al., 1991; Cd/PO_4 ratio calculated from their table 1) and are confirmed by our present data (Fig. 9). Otherwise the phosphate values as reported by Frew and Hunter (1992) appear about 10% higher than at nearby Geosecs stations, this would tend to produce the low Cd/phosphate ratios as reported.

Kremling (1985) and Kremling and Pohl (1989) studied this Cd–phosphate behaviour in North Atlantic surface waters. The latter authors observed distinct differences in the actual Cd concentrations during summer and winter situations in offshore waters. They reported a surplus of Cd vs. phosphate in nutrient-depleted waters, which is in contrast with our findings. Kremling (1985) observed both situations in Atlantic waters, he found Cd depleted waters with detectable phosphate concentrations as well as nutrient "exhausted" waters with rather high Cd concentrations. This may indicate that the uptake rates of Cd and phosphate are not only dependent of latitude, but also on the actual concentration and source of Cd and phosphate, as well as on the biomass and species composition of the plankton community. Recently, Saager et al. (1992) raised this point for the Indian Ocean. Obviously even on a small scale the uptake of Cd and phosphate by algae can differ dramatically, and is currently not well understood.

Zn

Zn (Fig. 6) shows similar behaviour as Cd but then more in relation with silicate than phosphate, as reported previously for other areas (Bruland, 1980; Yeats and Campbell, 1983; Danielsson et al., 1985). Surface concentrations of Zn range from 1.4 to 12.4 nM, increasing with depth to 7–15 nM at 300 m depth. The lowest values are found in the Scotia Sea, consistent with observations of Martin et al. (1990) at the same salinity and silicate concentrations. Latter authors reported low Zn (0.63 nM) concen-

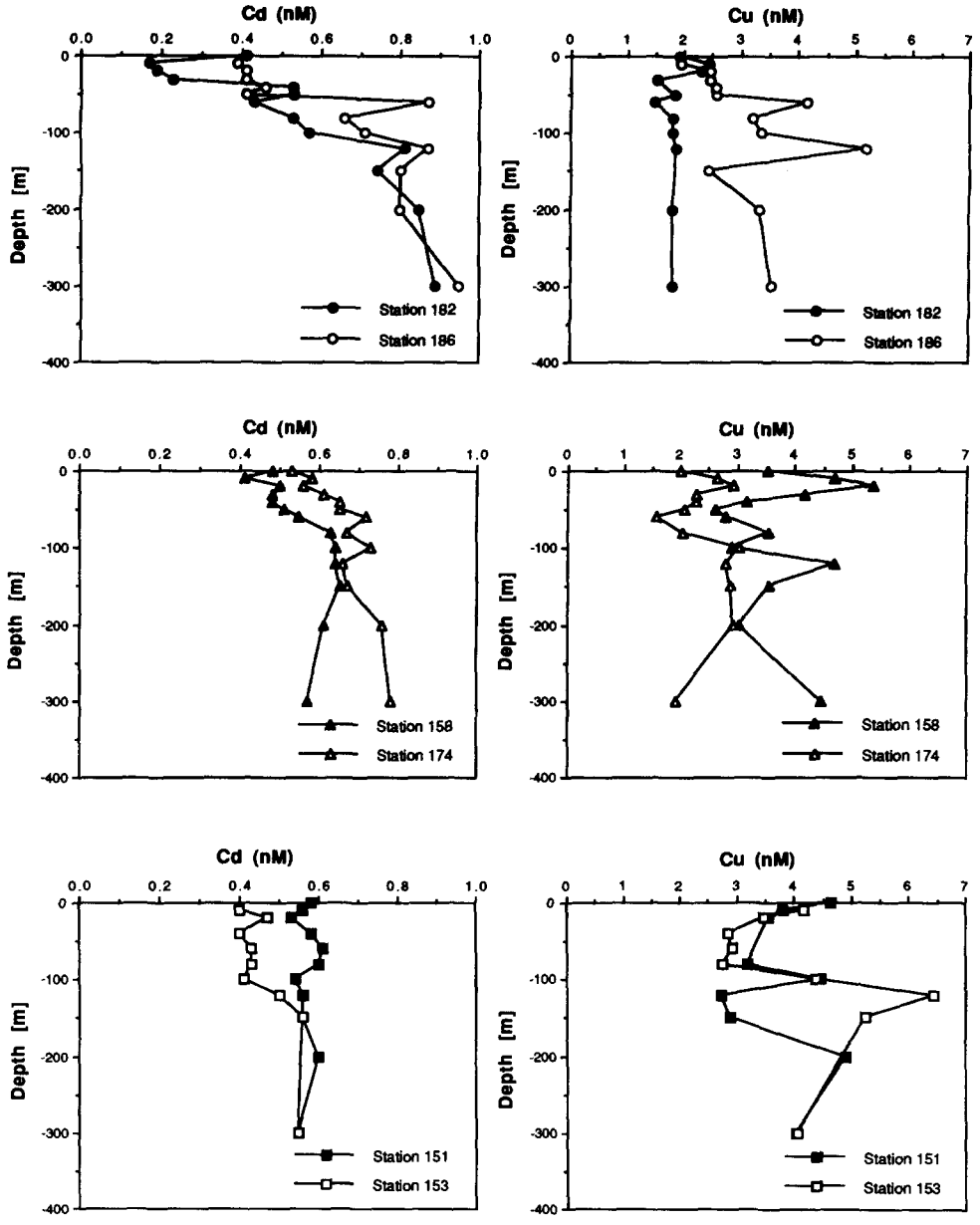

Fig. 6 Profiles of Cd, Cu, Zn and Ni (nM). For locations of stations see Fig. 2.

trations in the Drake Passage increasing in a southern direction with concentrations of 5–6 nM in the Gerlache Strait. Our observations show the same trend (Fig. 7), with even higher Zn concentrations in more southern direction. It is possible that water flowing through the Gerlache Strait in a northeasterly direction picks up extra Zn, but, on the other hand, analytical contamination can never be ruled out completely.

Below 100 m the highest Zn values are found in the Confluence and Weddell Sea. The existence of a relationship between Zn and silicate in the Weddell Sea was also reported by Westerlund and Öhman (1991b); however, with a poor relation on the whole data set. Even when these

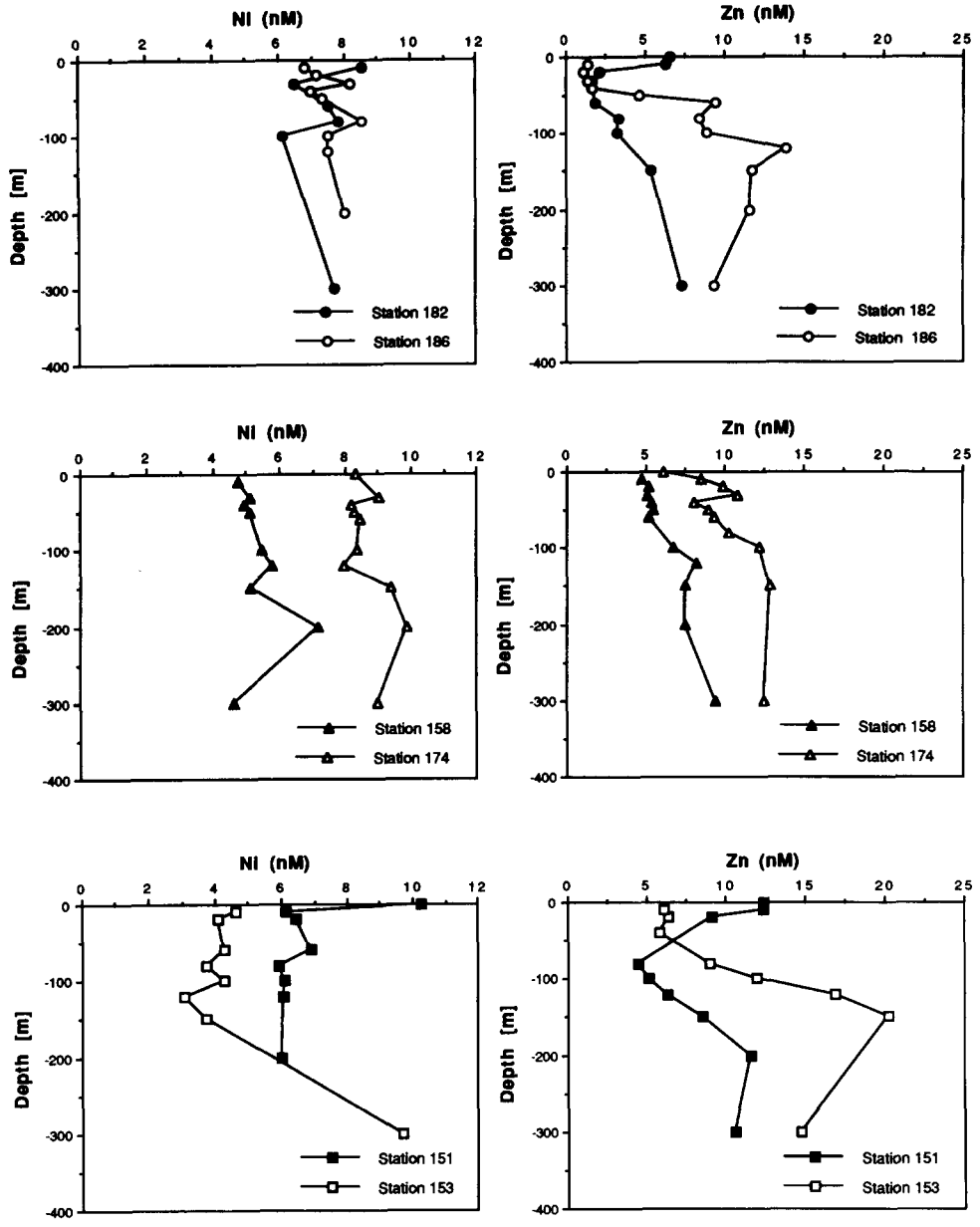

Fig. 6. (Continued).

authors separated surface waters from deeper, different source waters, this did not give a better relation. Our relation in surface waters for all data is given in Fig. 10. The overall equation is:

$$\mathrm{Zn\,(nM)} = 0.10\,\mathrm{Si}\,(\mu\mathrm{M}) + 0.94$$
$$(R = 0.64, n = 55)$$

The slope of this relation is intermediate between those in the western North Atlantic (0.17; Yeats and Campbell, 1983) and the Pacific Ocean (0.053; Bruland et al., 1978; Bruland, 1980). Orren and Monteiro (1985) reported Zn–silicate ratios in the southern Indian Ocean ranging from 0.16, at the most southerly stations, to 0.99 in northward direction.

Closer Zn/silicate relations are obtained when stations 182, 186 and 158 are separated from the

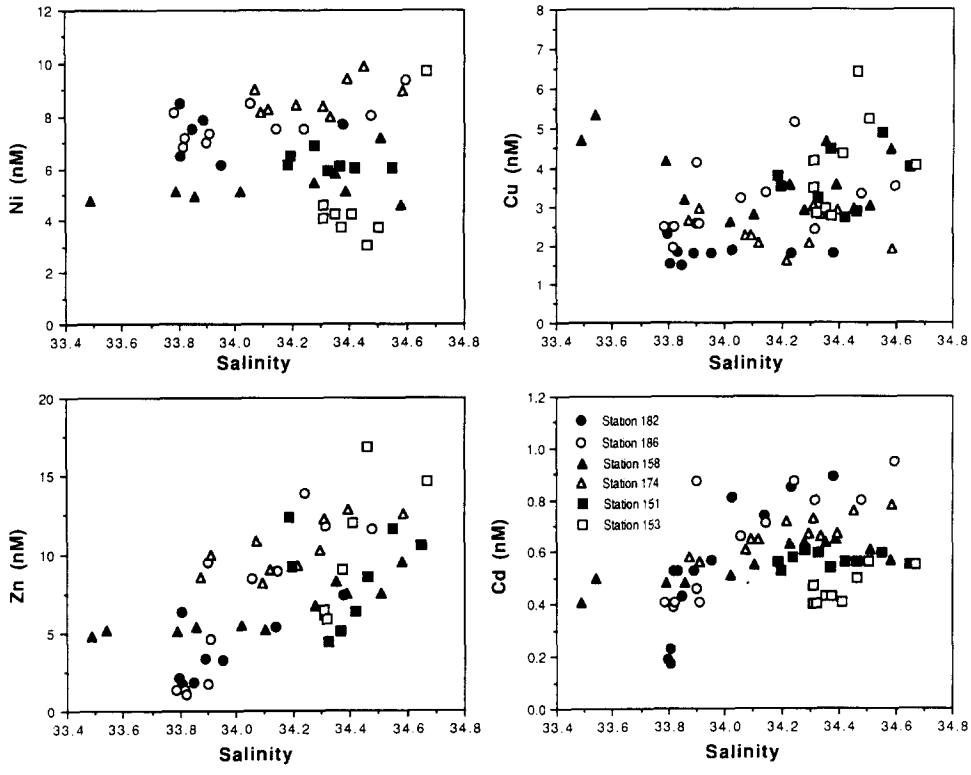

Fig. 7. Relation between salinity and Cd, Cu, Zn and Ni (nM). For locations of stations see Fig. 2.

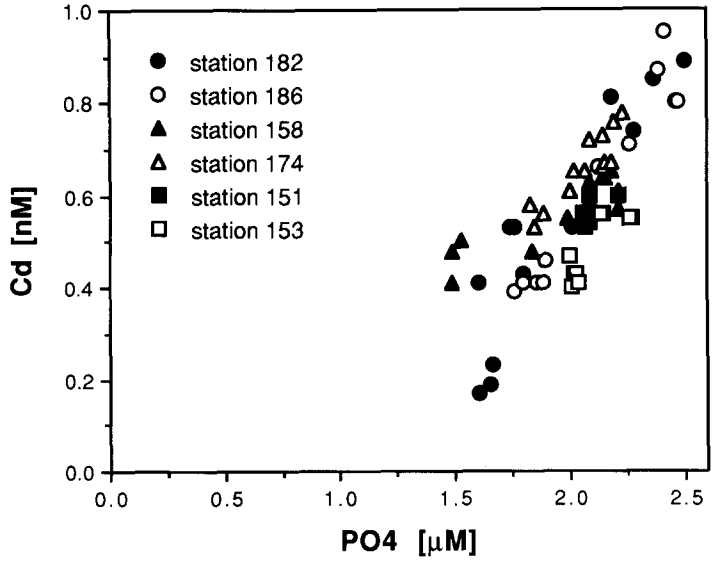

Fig. 8. Cd phosphate relationship in the three different areas. For locations of stations see Fig. 2.

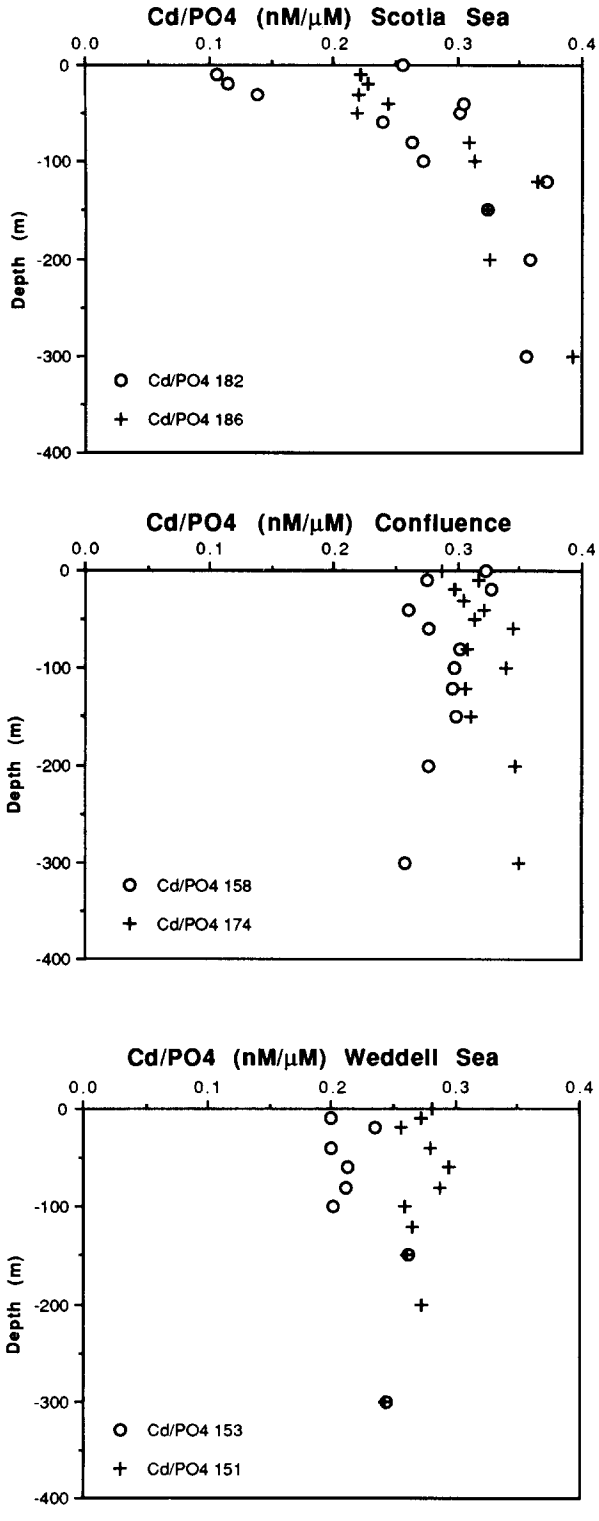

Fig. 9. Cd phosphate ratio (nM/μM) against depth in the Scotia Sea, Confluence and Weddell Sea.

others. These are the stations where biological activity is highest, indicated by the lowest nutrient concentrations. Here we get correlation coefficients of 0.90 and higher. The covariance between Zn and silicate is clearly indicated in the Confluence where both high Zn and high silicate concentrations are found at station 174, in contrast to lower levels at station 158 (Figs. 5 and 9). Especially in the Weddell Sea, the relation is very weak, not in the least due to the small variation in the silicate content (Fig. 5). The heterogeneity in this area may be due to the melting of ice, snow and icebergs. This may contribute considerable amounts of Zn to the seawater (Westerlund and Öhman, 1991b). This was shown by Boutron et al. (1990) reporting zinc concentrations in ancient ice from Antarctica ranging from 0.15 to 1.5 nM. Westerlund and Öhman (1991b) reported Zn concentrations in Antarctic snow samples of about 5 nM, ranging from 4 to 10 nM. However, for the highest Zn values analytical contamination again cannot be excluded. In the Scotia Sea, Zn and silicate concentrations are more regulated by biological uptake, as also seen for Cd and phosphate. The differences in slope and intercepts for both the Cd–phosphate and the Zn–silicate relations in the three studied regions indicate that the uptake and release of these elements in the biogeochemical cycle is very complex. Within each region distinct trends vs. nutrients are found, but the apparent variation between regions precludes combination into one overall trend (Figs. 9 and 10).

Cu

Depth profiles of Cu (Fig. 6) do not show lower concentrations near the surface. In the Scotia Sea proper (station 182) the concentration gradient of Cu is very small in the upper 300 m. This concentration (~ 1.8 nM) is somewhat (~ 0.3 nM) higher than the Cu results reported by Martin et al. (1990) from the Drake Passage. At the other stations in the Confluence and Weddell Sea, Cu concentrations ranged from 2 to 5 nM. These values are somewhat

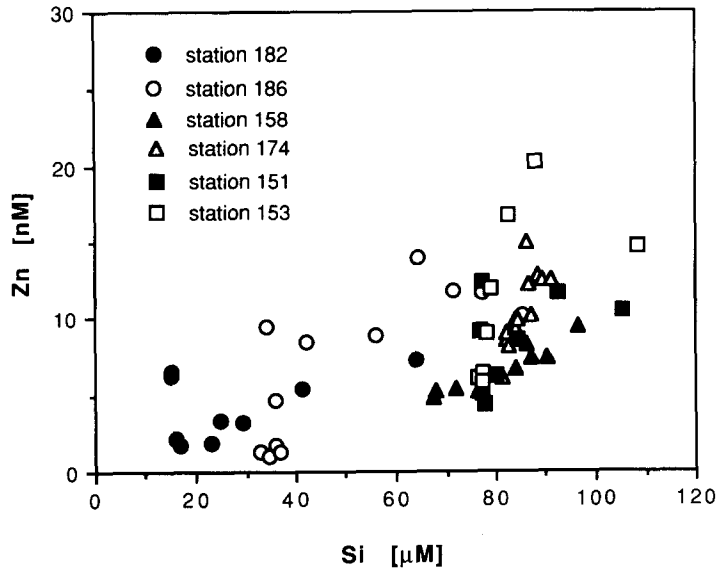

Fig. 10. Zn silicate relationship in the three different areas. For locations of stations see Fig. 2.

higher than those reported by Westerlund and Öhman (1991b), considering our results from stations 151 and 153 in the Weddell Sea. If this is due to contamination, a possible source can be the research vessel which can obscure the surface Cu concentrations at these stations. When the ship creates an open place in the ice, which is done by breaking it, there may be some release of Cu from the ship. However, when comparing the 10 m depth samples near the ship with the very surface water values (0 m) taken with a zodiac far away from the ship (Nolting et al., 1991, table 2), there is no significant difference in the admittedly small dataset.

On the other hand, at station 174 in the Confluence, where the ice cover was absent, Cu concentrations are in the same range as those reported by Westerlund and Öhman (1991b).

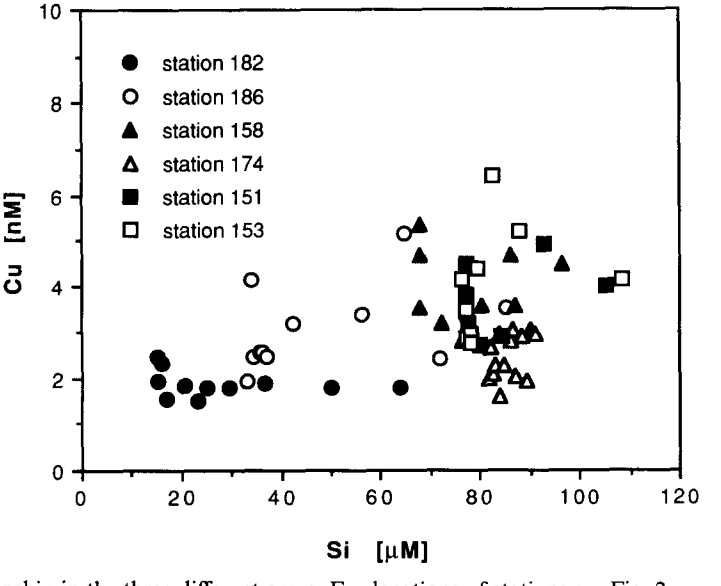

Fig. 11. Cu silicate relationship in the three different areas. For locations of stations see Fig. 2.

The relation between Cu and silicate at this station (Fig. 11) shows a cluster, due to the small concentration gradient of both elements.

It is obvious that the Cu concentrations in the surface waters at these latitudes are higher than in the temperate ocean at mid-latitudes. Especially the high silicate indicates an upward transport of bottom waters rich in silicate and Cu. Subsequently this water mixes with surface waters of the Weddell Sea gyre and shallow waters derived from the Gerlache Strait and Bransfield Strait. In Fig. 11 the relation between Cu and silicate in the surface waters is shown. The correlation is very weak. Nolting et al. (1991) noticed the anomaly of Cu vs. silicate when comparing Scotia Sea surface data with North Atlantic surface data. Apparently, nutrient-rich surface waters do not show a good relationship between Cu and silicate, as noted earlier by Bruland (1980). As a matter of fact, Kremling (1985) did not find a relationship between Cu and nutrients for nutrient-depleted surface waters either. Presumably a good relation between Cu and silicate can only be found when deep water values are included.

Interactions with the formation and dissolution of opal can also influence the actual copper concentrations. Westerlund and Öhman (1991b) found a good relationship between Cu and silicate in their samples from the Weddell Sea. They suggested that opaline particles are a dominant carrier of Cu. Another possibility is that release of copper from ice-algae, together with a poor vertical mixing in the ice-covered waters, dictates the Cu distribution. As soon as the ice has retreated and the wind-mixed layer increased, the Cu distribution in the surface layer becomes more homogenous as can be seen with the results of station 174 (Fig. 11). Otherwise it is evident that the Cu–silicate and Zn–silicate relations show more or less the same regional trend.

Ni

The depth profiles of Ni (Fig. 6) show a concentration range of 4 nM in the Weddell Sea (the most southern point) to 8 nM in the Scotia Sea. In contrast to this horizontal trend, the vertical variation at each station is rather small. Below 200 m, the Ni concentration at station 153 tends to increase, but because this is only one point it is not clear if this is a real increase. It seems that the Ni distribution in the whole area can be separated in two different parts (Fig. 7). The southern part, with an ice cover, exhibits concentrations between 4 and 6 nM, whereas in the northern ice-free part concentrations range from 6 to 10 nM. Concentrations of Ni published by Westerlund and Öhman (1991b) for the Weddell Sea, between 5 and 7 nM, are in good agreement with our results. The lower 4 nM Ni concentration at station 153, correlates with the low phosphate concentration at this station (Fig. 5).

However, a clear correlation of Ni with any nutrient is not found. The absence of any correlation of Ni with nutrients in the Weddell Sea was reported before by Westerlund and Öhman (1991b). It is possible that the ice-covered part of the water body prevents the mixing of surface water with a lower Ni content, with deeper water with a higher Ni content, as shown by Nolting et al. (1991, fig. 4).

The higher Ni concentrations in the Confluence and Scotia Sea are in the same range as those reported by Bruland (1980) for the deep north Pacific Ocean. As noticed earlier the waters in these regions are mostly derived from the Drake Passage and the Gerlache Strait and may have been transported more southward as ice receded. So, the source of the higher Ni concentrations in the northern area, compared to that in the Weddell Sea, could be Pacific waters. Uptake of Ni from marginal sediments by waters flowing through the Gerlache Strait, similarly as suggested for Zn, is another possibility. Unfortunately no other Ni data from this area are available for comparison.

5. Conclusions

The surface waters (upper 300 m) in the Scotia Sea, Confluence and Weddell Sea are not only

characterized by different temperature and salinity regimes, but also by their nutrient and trace metal concentrations. The Confluence is clearly a transition area between the Scotia and Weddell Sea. In addition the receding ice-edge (time of sampling, plankton bloom), preventing mixing of the surface water layer, has a major impact on trace-metal distributions.

Surface salinities are highest in the Weddell Sea and decrease in northward direction. Only when there is a direct influence of melting ice, the local salinity is lower than in the surrounding waters. The reverse is found for the temperature, being lowest in the Weddell Sea and highest in the Scotia Sea with a distinct minimum at 75 m depth. Below 100 m, phosphate and nitrate concentrations are highest in the Scotia Sea, yet in the first 100 m lower than in the Confluence and Weddell Sea, due to biological uptake. These differences have virtually no impact on their inter-relationship, which is rather constant at a Redfield ratio of 14.6; however, there are small deviations discernible in the different areas. Silicate has clearly lower concentrations over the whole 300 m in the Scotia Sea compared to levels in the Confluence and Weddell Sea.

Cd concentrations are high compared with other surface waters, but the correlation with phoshate as found in other oceans is still strong. The highest Cd concentrations are found in the Scotia Sea gradually decreasing towards the Weddell Sea. Despite this strong correlation between Cd and phosphate there are some slight differences in the different areas when plotting the Cd/phosphate ratio with depth. This indicates that the utilization of Cd and phosphate is approximately the same both in the Confluence and in the Weddell Sea. Yet, in the Scotia Sea the removal of Cd from the surface layer is faster than that of phosphate, or phosphate is faster mineralized in the first 100 m compared to Cd.

Zn shows a good relationship with silicate but when calculated for each region on its own, much better relationships were found. This indicates that, in this complex area, the Zn–silicate ratio is specific for each region, and depends on biological uptake rates and an extra input of Zn due to melting ice. Higher Zn concentrations in the Confluence can be due to release from bentic sources.

Cu does not show lower concentrations near the surface layer as do Cd and Zn. However, there are some fluctuations in the vertical profiles and it is evident that the highest concentrations are found in the Weddell Sea, which is in contrast to Cd but similar to Zn. For surface waters, no relation exists between Cu and silicate. This can be due to contamination problems but, especially in the Weddell Sea, the narrow range in silicate concentrations plays a role as well. When deep water data are included it must be possible to get a better fit, as shown by Westerlund and Öhman (1991) and Nolting et al. (1991).

The Ni concentrations appear to be rather constant in the first 200 m of each region, but the actual concentrations are different between regions. Especially in the ice-covered Weddell Sea and Confluence, concentrations of Ni are lower than in the Scotia Sea. In some occasions Ni shows covariance with phosphate, while in other cases this is more clear with silicate.

In general it can be concluded that the surface waters in the rather turbulent area near the Antarctic Peninsula, are separated by fronts. The surface waters divided by these fronts are not only specified by their salinity, temperature and nutrient properties, but also by different trace-metal concentrations. It is also shown that the concentrations of the different parameters in a given region are more dependent on the time of sampling than the exact sampling position.

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